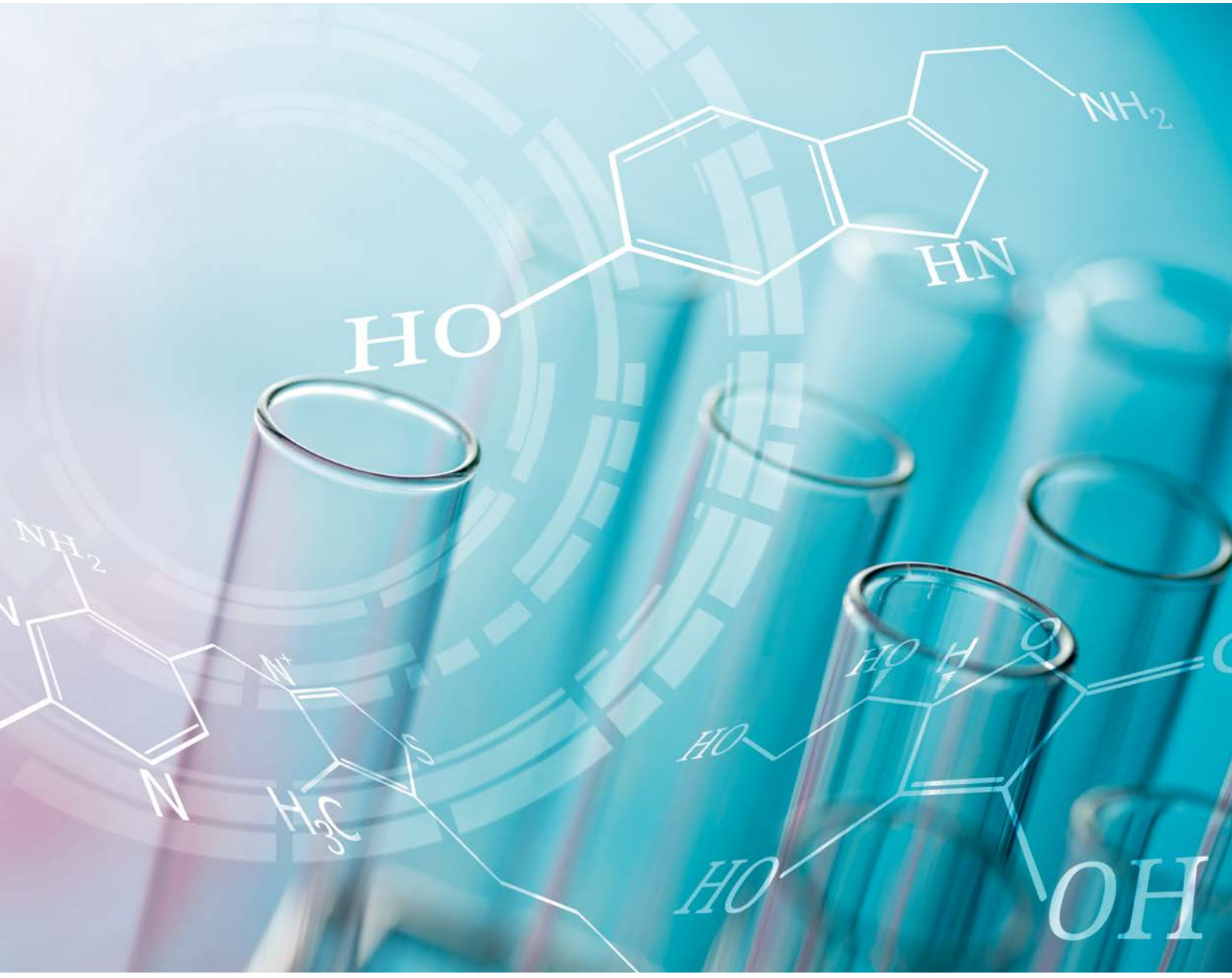
NETZSCH

Proven Excellence.



TGA-GC-MS Coupling

Evolved Gas Analysis with Chromatographic Pre-Separation

Analyzing & Testing

Thermogravimetry and

Thermogravimetry (TGA) and Simultaneous Thermal Analysis (STA)

Thermogravimetry (TGA) and Simultaneous Thermal Analysis (STA), which is primarily simultaneous TGA-DSC (Differential Scanning Calorimetry), are widely applied analytical methods for the research and quality control of all kinds of inorganic and organic materials and products. Often, it is not sufficient to determine only the mass and enthalpy changes resulting from a thermal treatment; additional information may be required about the volatile products evolved during chemical reactions, thermally induced transitions, evaporation, and decomposition in order to gain deeper insight into the nature, structure and composition of the materials.

NETZSCH thermobalances and STA systems are arranged vertically with the sample above the balance, allowing the gases to flow in the natural upward direction. This design is ideal for coupling gas analysis equipment to the top of the furnace.

Mass spectrometry (MS) is the most comprehensive method for gas analysis, providing sensitivity down to the ppb/ppm level, high resolution at the atomic level, and also high speed of detection. Although the direct coupling of quadrupole mass spectrometers (QMS) – e.g., *Aëolos* or *SKIMMER* to a TGA or STA – is a well proven method, it has limitations in determining the individual components of gas mixtures which often hinder clear identification and interpretation. This is where gas chromatography comes into play.

TGA/DSC Information*

- Dehydration
- Desolvation
- Binder burn-out
- Decomposition
- Pyrolysis
- Combustion
- Oxidation
- Corrosion
- Evaporation
- Compositional analysis
- Ash content
- Melting/Crystallization
- Solid-solid transitions
- Glass transition
- Specific heat capacity

* For more information, please see STA *Jupiter*® brochures.

TG 309 *Libra*®-GC-MS

Evolved Gas Analysis

Gas Chromatography (GC) – Mass Spectrometry (MS)

GC is a high-resolution method for separating volatile and semi-volatile compounds. The gas mixtures are separated based on the differences in component distribution between a stationary phase (e.g., inner coating of a capillary) and a mobile phase (purge gas; e.g., helium).

Gas components with low affinity for the stationary phase but higher affinity for the mobile phase will be rapidly carried away by the purge gas, whereas gases with a high affinity for the stationary phase will follow with a relatively significant time delay ("retention time").
MS is applied as a detection system at the outlet of the GC separation column and will register the time distribution of the separated gas components in the purge gas flow. Because of this pre-separation of the gases by the GC, and the sensitivity and resolution of the MS, detailed structural information is provided, allowing most compounds to be identified exactly.

Mobile Phase

The mobile phase in GC is a gas, therefore all analytes must be evaporated and introduced into the column in gaseous form.

Stationary Phase

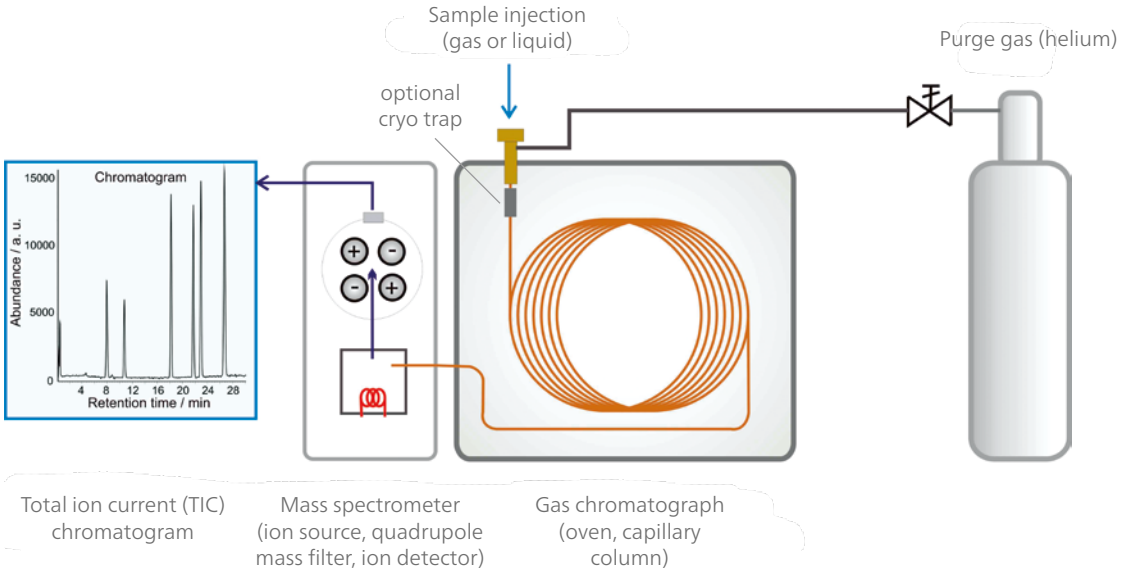
In current technology, the stationary phase in the GC is usually a polymeric coating inside a long and narrow fused silica capillary.

GC-MS Information

- Solid-gas reaction
- Decomposition products
- Pyrolysis gases
- Combustion products
- Flue gas identification
- Separation of complex gas mixtures
- Gas detection and identification
- Compositional analysis
- Identification of additives (e.g., plasticizers)

TGA/STA-GC-MS Coupling

Since the gas separation in the GC column takes a certain amount of time – the duration of which depends upon sample characteristics, column flow rate, column length, and stationary and mobile phase – it is not possible to couple into the GC with a continuous online sample gas flow. Our solution, therefore, was to develop a direct coupling in a quasi-continuous mode using heated automatic valves, which allow for software-controlled gas sampling (flow-through sampling loop) and gas injection, even at short intervals, within the NETZSCH *Proteus*® software.



The injected gas mixture of the sampling loop (or parts of it in the split mode) passes the separation column of the GC under the flow conditions set (e.g., constant flow of the purge gas at 1.5 to 2 ml/min) and arrives, after a final pressure reduction step, as a molecular beam at the ion source of the quadrupole mass spectrometer. The separation column is either held at a constant high temperature (for the quasi-continuous injection mode), or temperature-programmed from a low start temperature to a subsequent high temperature (for the event-controlled mode). The mass spectrometer detects all volatile products and records them as a function of time. The curve of the total ion current (TIC) over time (retention time) is called a chromatogram. Peaks appear in the chromatogram resulting from the sample gas interaction in the stationary and mobile phases, and from the boiling temperatures of the individual components. These retention peaks are analyzed by the MS software to determine the contributing substances.

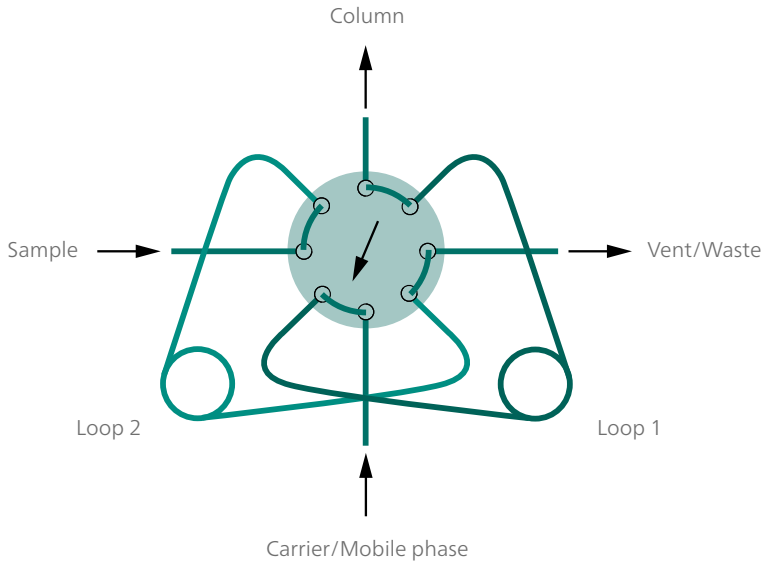
Valve Box

The NETZSCH valve box contains a heated double loop system. Operation of the valve is completely controlled by the NETZSCH *Proteus*® software. This system allows either continuous injections (i.e., recurrent injections at defined intervals and with a definable number of occurrences) to the GC column or event-controlled injections.

Maximum Flexibility

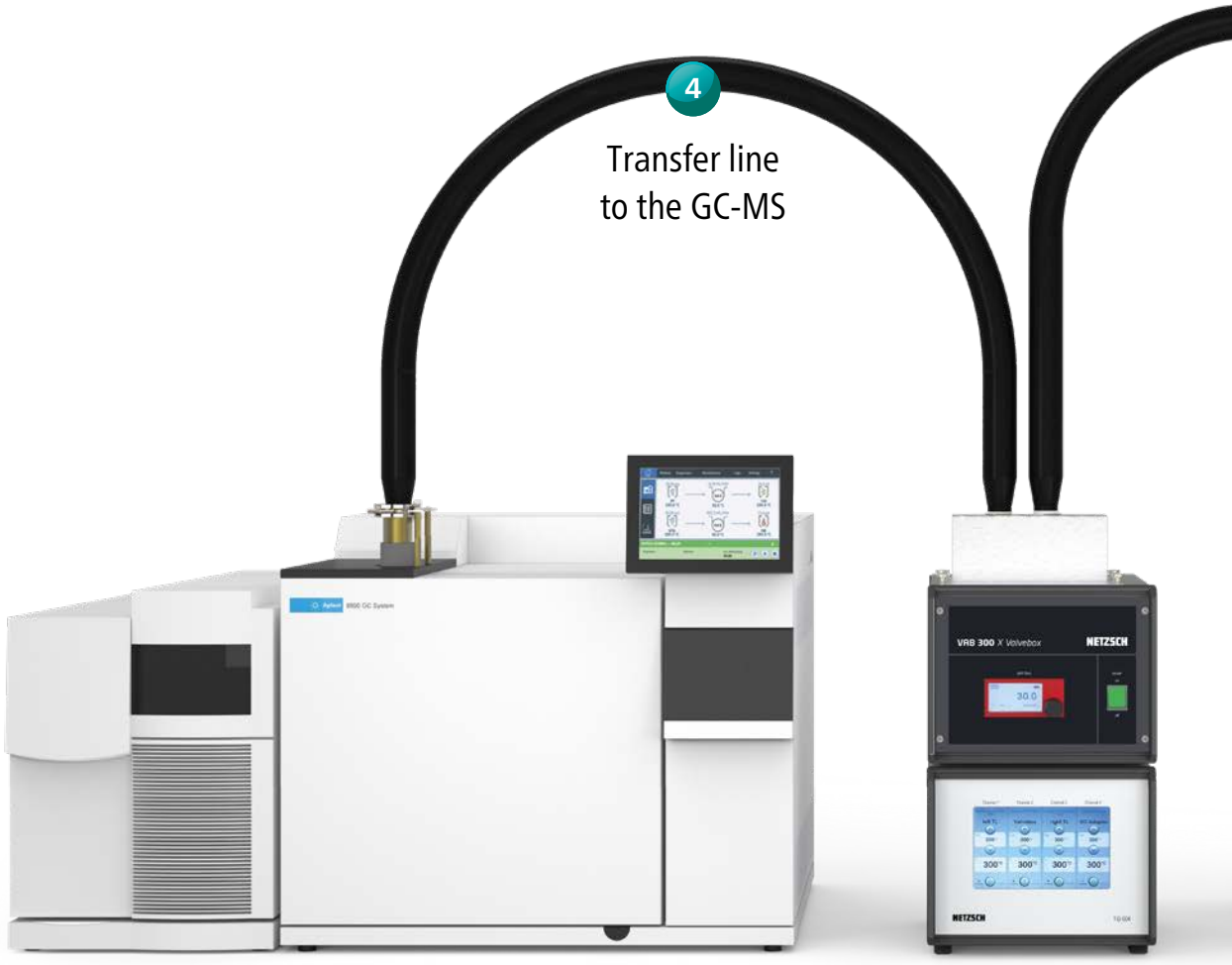
To achieve a higher concentration in evolved gas species, an optional cooling trap can be placed between the injector system and the GC column.

Additionally, it is also possible to directly inject the gas mix into the mass spectrometer, bypassing the GC column.



TGA/STA-GC-MS Coupling

Gas chromatography comes into play when MS has reached its limitations in determining the properties of complex gas mixtures.



1 Mass spectrometer

2 Gas chromatograph

3 Valve-based gas injector and temperature controller

5 STA 509 *Jupiter*®

1 Mass Spectrometer (MS)

- State-of-the-art Quadrupole-MS
  - >1000 u
  - High-speed sampling; up to 20000 u/s
  - Various ionization techniques available (EI, CI, PI, depending on MS type)
- Tool-free servicing, e.g., simplified ion source maintenance
- Stand-alone MS measurements

2 Gas Chromatograph (GC)

- Split, splitless, pulsed split injection modes
- GC furnace up to 450°C
- Fast change of column without venting the MS (option)
- Multiple columns available for specific applications

3 NETZSCH Box – Valve-Based Gas Injector

- Double-loop system for short injection intervals
- Software integrated in *Proteus*®
- Special insulation design for constant temperature (up to 350 °C) to prevent cold spots
- Easy GC integration via standard S/SL injector
- Quick connection too allow fast switch between TG coupling and standard application (e.g. liquid sampling)
- Possible to bypass the column for direct MS coupling
- In-build flow control system to ensure reliable gas transfer

4 Transfer System

- Heated adapter system (up to 400°C)
- Heated transferline (max. 350 °C) with inert glass-lined steel capillary

5 Customizable Thermal Analyzer (TGA/STA)

- Variable furnaces for a broad temperature range
- Various sensors
- Automatic sample changer with capacities of between 20 and 192 sample pans, depending on instrument
- Bypass system for excess gas
- Simultaneous coupling of TGA/DSC-GC-MS-FT-IR

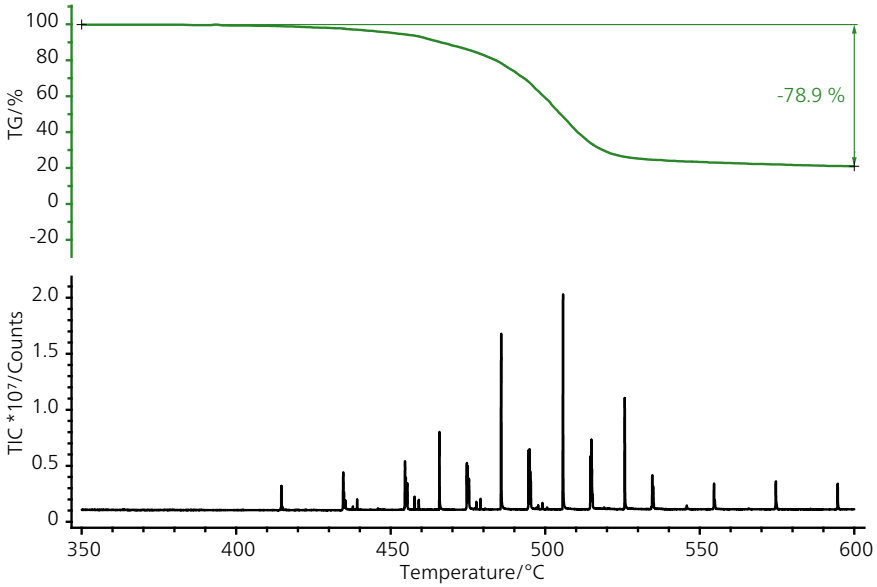
THE THREE MEASUREMENT MODES

QUASI-CONTINUOUS, EVENT-CONTROLLED AND CRYO TRAP

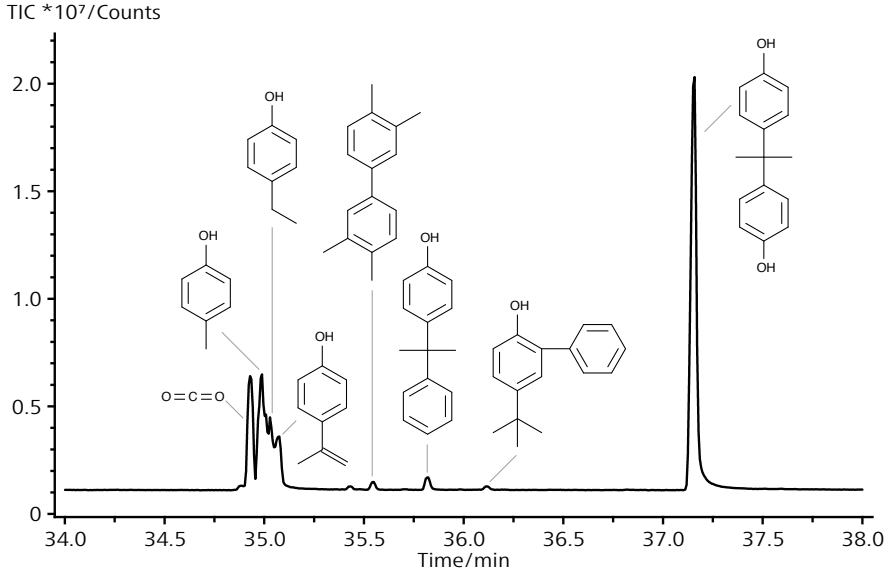
ARE EXPLAINED WITH THE HELP OF THE SAME MATERIAL: POLYCARBONATE (PC)

Quasi-Continuous Mode – Pyrolysis of Polycarbonate (PC)

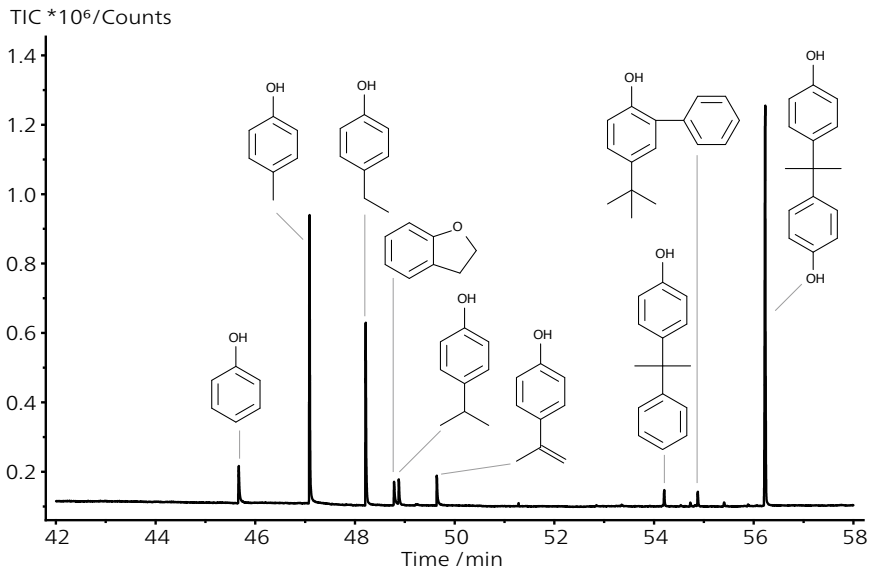
During the entire TGA run, the gases produced were sampled at intervals of 4 min in the GC column, which was kept at a constant temperature of 200°C. As soon as the mass loss started, the total ion current (TIC) detected several peaks. Analysis of the MS spectra for each injection gave a mixture of compounds released during pyrolysis. Eight different compounds were identified. Due to the increased temperature of the column, not all peaks were separated perfectly.



TGA measurement of polycarbonate (PC) in correlation to the corresponding total ion current in the continuous mode



Enlarged view of the total ion current between 34 min and 38 min; peaks labeled with identified compounds

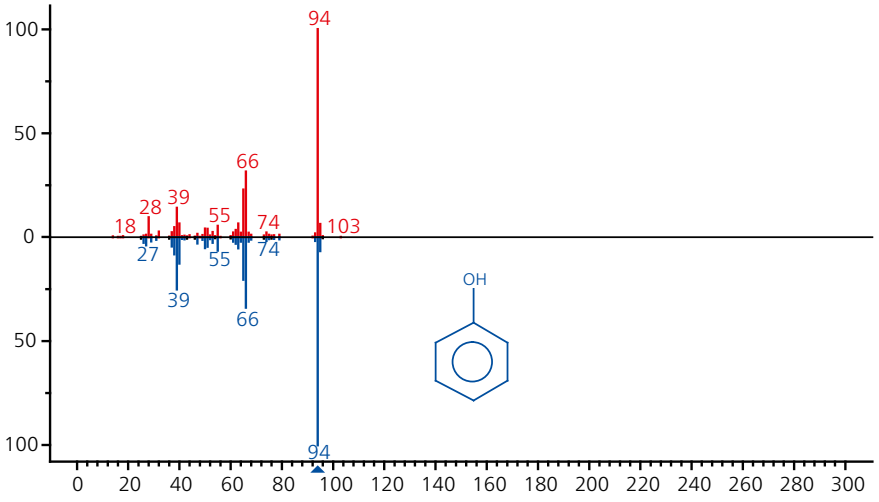


Total ion chromatogram for polycarbonate measured in the event mode; peaks labeled with identified compounds.

Event-Controlled Mode

One injection to the column was automatically conducted as soon as the DTG peak (peak in the first derivative of the TGA curve) was detected by the software. The GC column was heated from 40°C to 300°C at 5 K/min to separate the compound mixture. Nine compounds could clearly be identified. To do so, the mass spectra of each peak were compared to the NIST library. The identification of phenol is shown below as an example.

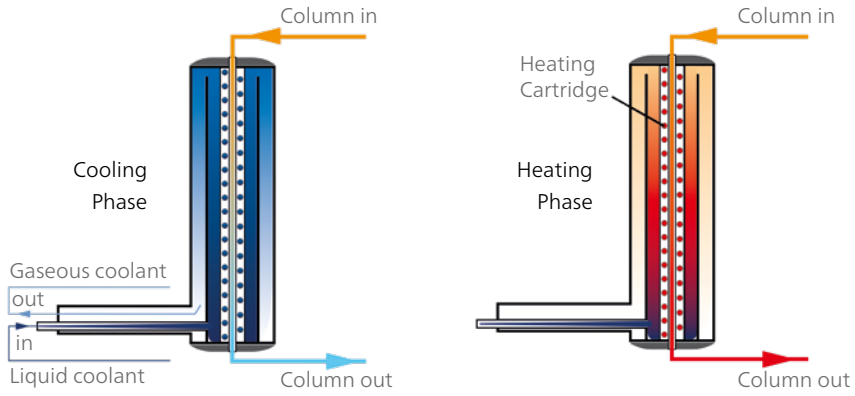
RT (min)	Score	Name
38.900	93.2	CO_2
45.669	94.1	Phenol
47.089	96.1	4-Methylphenol
48.216	96.3	4-Ethylphenol
48.783	86.6	Dihydro-Benzofuran
48.878	90.0	Isopropylphenol
49.642	93.7	Isopropenylphenol
54.205	86.8	Phenol, 4,4'-(1-methylethylidene)bis-
54.879	81.5	Phenol, 4-tert-butyl-2-phenyl-
56.233	94.6	Phenol, 4-(1-methyl-1-phenylethyl)-



Measured mass spectrum at 45.669 min (red) compared to the NIST library spectrum for phenol (blue)

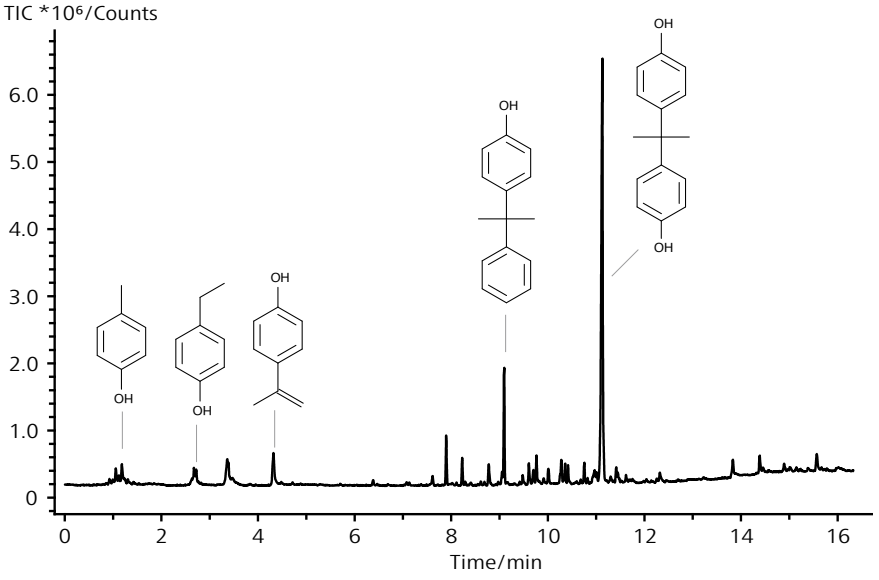
Multi-Injection and Cryo Trap Mode

During the TGA measurement, the outer jacket of the cryo trap is cooled with liquid nitrogen to trap outgassing compounds (cooling phase, left image) to increase concentration. After the gas collection has completed, the trap is immediately heated with the built-in heating cartridge (heating phase, right image) at high heating rates to ensure sharp gas injection to the column.

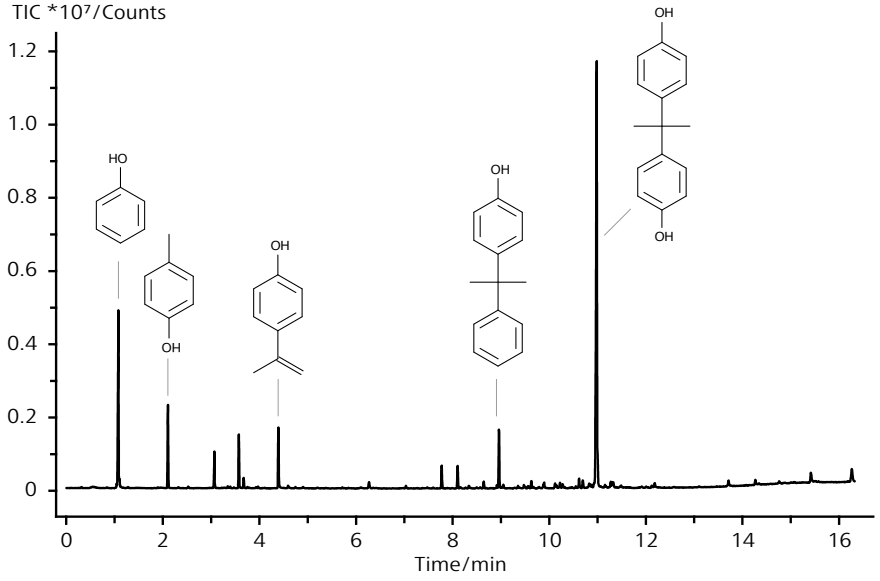


Functional principle of the cryo trap

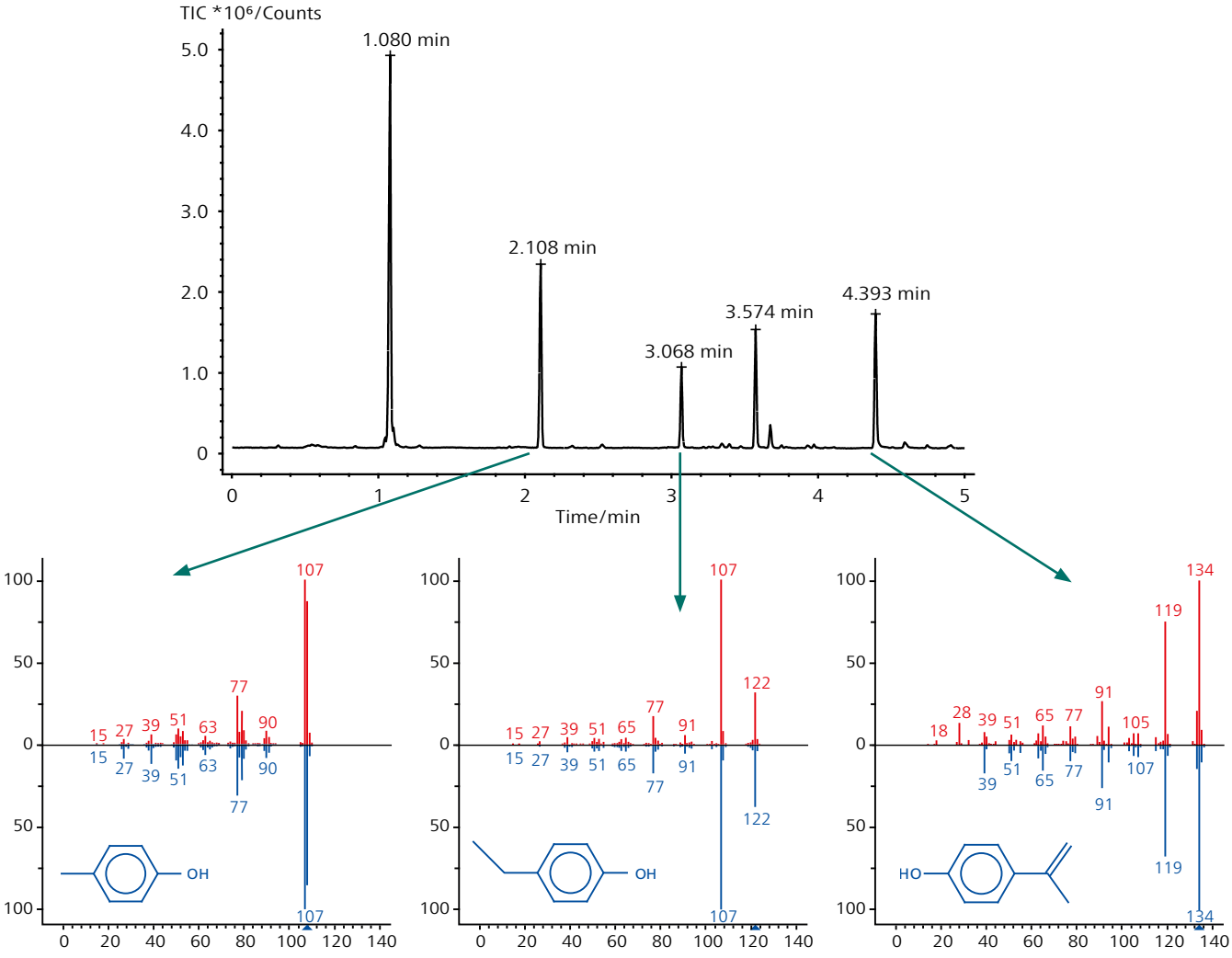
In principle, the detection limit of by-products can be increased by sampling the gases during the TGA measurement on the cold column (40°C) at very short intervals (multi-injection approach) and then analyzing them by dynamically heating the GC column.



For the cryo trap approach, the gases are collected at -50°C. Compared to the pure multi-injection approach, this lower condensation temperature leads to improved condensation of the gas on the column. The chromatogram obtained clearly shows sharper peaks and allows for improved analysis of the gas mixture.



Evaluation of the GC-MS-TIC Chromatograms



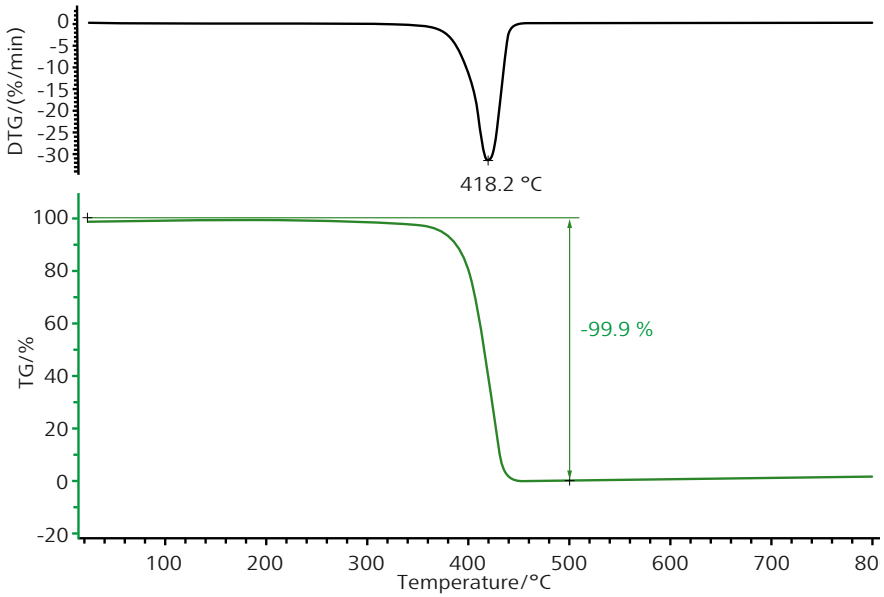
RT (min)	Score	Name
1.080	95.31	Phenol
2.108	96.79	Phenol, 4-methyl-
3.068	92.00	Phenol, 4-ethyl-
3.574	92.30	Benzofuran, 2,3-dihydro-
3.675	93.31	Phenol, 3-(1-methylethyl)-
4.393	93.36	p-Isopropenylphenol
6.269	85.55	Phenol, 2,4-bis(1,1-dimethylethyl)-
7.774	95.52	Diphenyl carbonate
8.105	72.62	Pyridine, 2,3,4,5-tetramethyl-6-phenyl-
8.959	88.71	Phenol, 4-(1-methyl-1-phenylethyl)-
9.627	77.86	Benzene, 1-(1,1-dimethylethyl)-4-phenoxy-
9.896	74.97	Benzo[b]-1,8-naphthyridin-5(10H)-one,10-methyl-
10.222	78.61	Phenol, 4-(2-phenylethenyl)-, (E)-
10.621	83.00	4,4'-Ethylidenediphenol
10.694	72.64	1-Methoxy-6-methylphenazine
10.986	88.79	Phenol, 4,4'-(1-methylethylidene)bis-

The GC-MS software enables easy evaluation of the mass spectra for each peak in the chromatogram. An easy zoom-in function allows for enlargement of the peaks. The NIST search generates a compound list including retention time, score and compound name. Each measured spectrum can be displayed in comparison to the NIST spectrum.

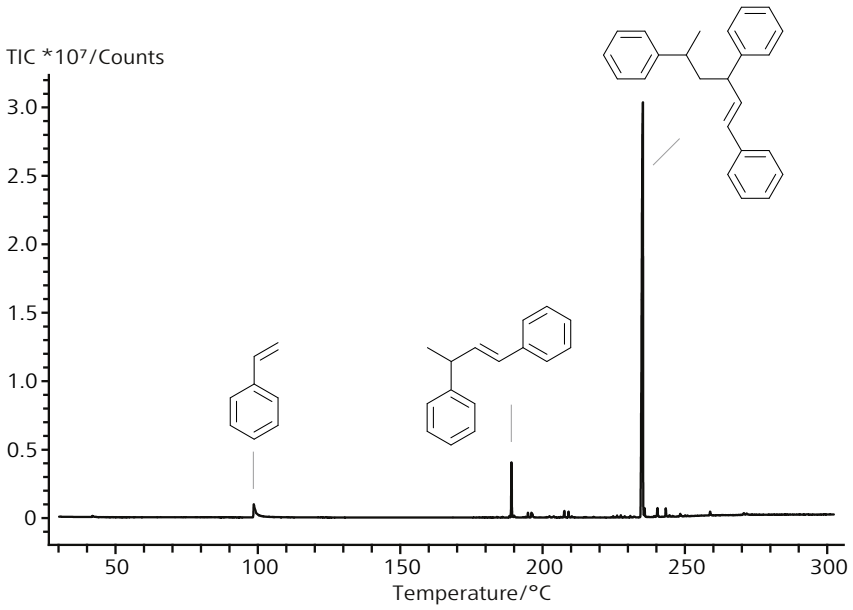
Unlimited Applications

Pyrolysis of Polymers

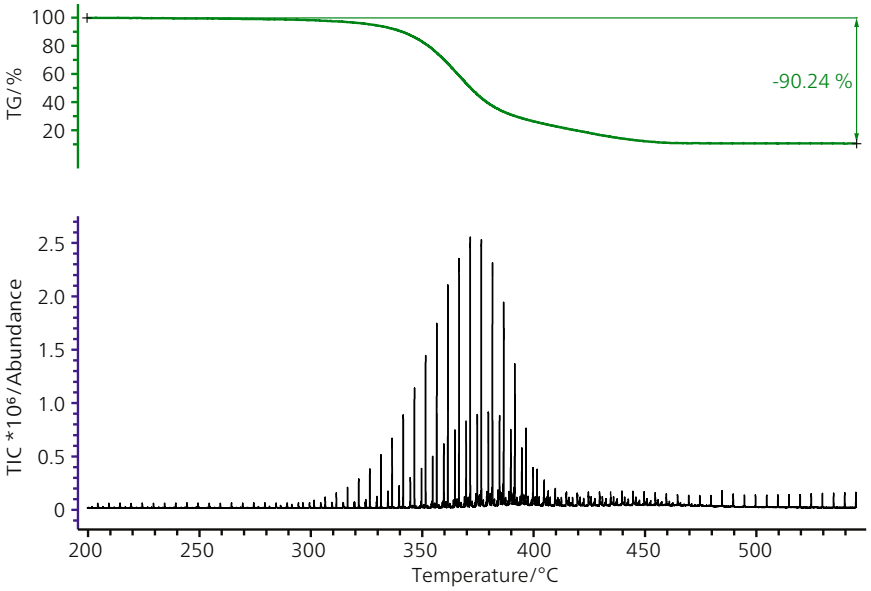
This example shows a thermogravimetric measurement (TGA, green) on polystyrene with the event-controlled mode. One gas portion was injected on the column at the DTG peak (black) at 418°C. Separation of the compounds released over the GC column with a temperature ramp of 15 K/min yielded the three main compounds styrene, the styrene dimer and styrene trimer, which are in good correlation with literature data.



TGA curve (green) for polystyrene (PS) under inert conditions; mass loss rate (DTG, black)



Total ion chromatogram for polystyrene (PS), measured in the event mode; peaks labeled with identified compounds.

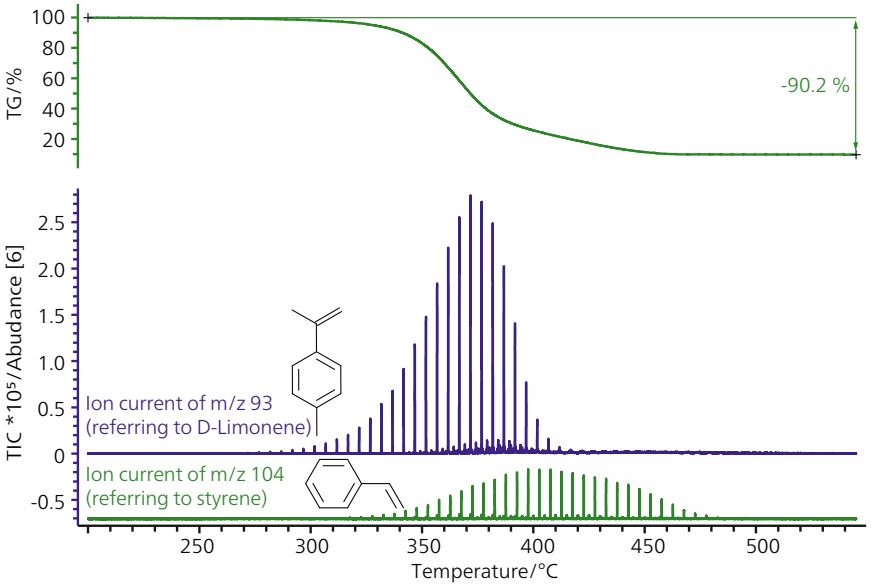


Temperature-dependent mass change (green) in correlation with the total ion chromatogram (TIC, black)

Mixture of NR and SBR

The rubber mixture was heated under inert conditions to 550°C at 5 K/min. The measurement showed one broad mass-loss step. The GC-MS experiment was performed in the quasi-continuous mode, sampling every 30 sec to the column with a temperature of 100°C.

The total ion current (TIC) shows the detected gases in the mass spectrometer during the mass-loss step. For each injection, several peaks in the TIC were detected. This means a simultaneous release of a mixture of compounds.

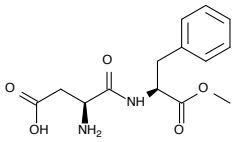


TGA curve (green) for natural rubber with an 8% styrene-butadiene rubber content in comparison with the mass numbers 93 for limonene and 104 for styrene.

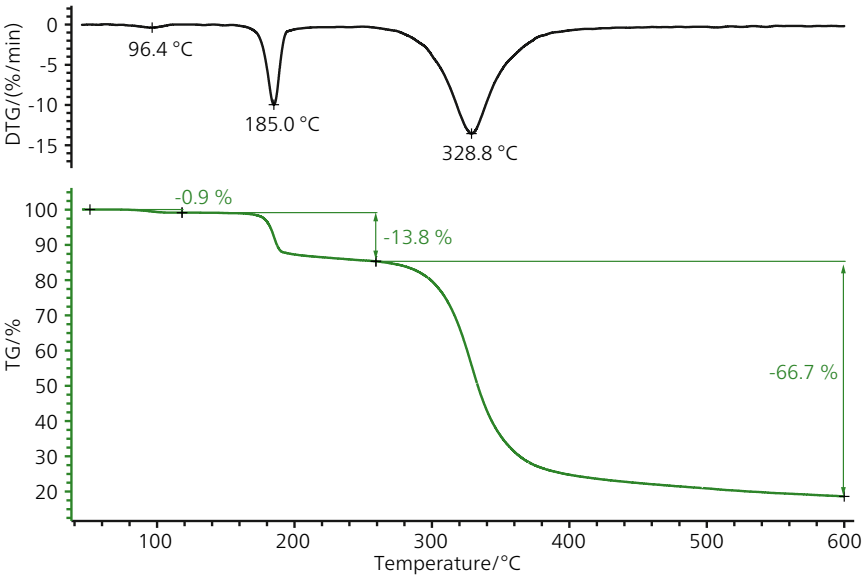
Mass number 93 was found to be specific to limonene, a pyrolysis product of NR. Styrene with mass number 104 was followed to show the pyrolysis of SBR. The individual ion current curves show good correlation with the mass change; additionally they show that SBR was pyrolysed over a larger temperature range than NR.

PHARMACEUTICALS

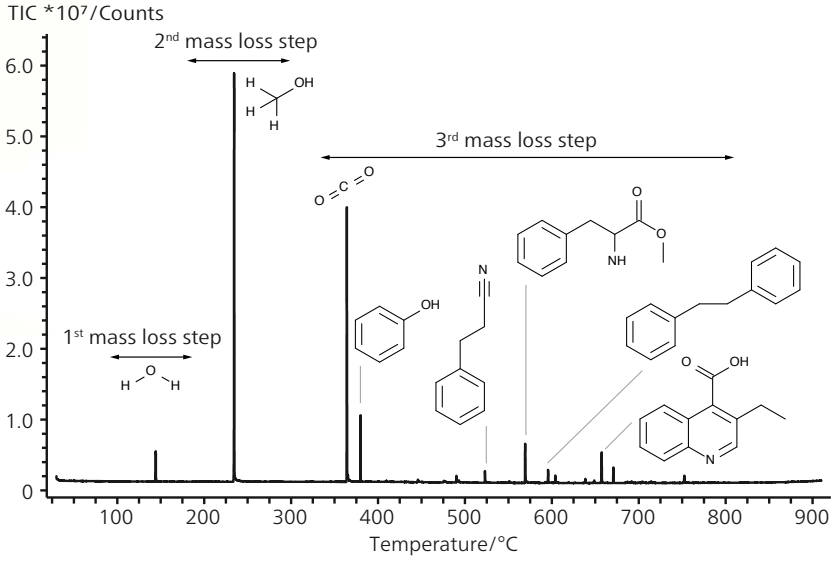
Aspartame



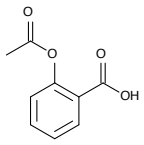
The common sweetener and pharmaceutical excipient was heated to 550°C to investigate thermal stability. Evolved gases were analyzed in the event-controlled mode. Every mass-loss step caused an injection to the GC column. The first mass-loss step resulted from the release of surface water. During the second mass loss, the ester was functionally cleaved and methanol was released. The third mass-loss step showed the formation of several aromatic fragments during pyrolysis.



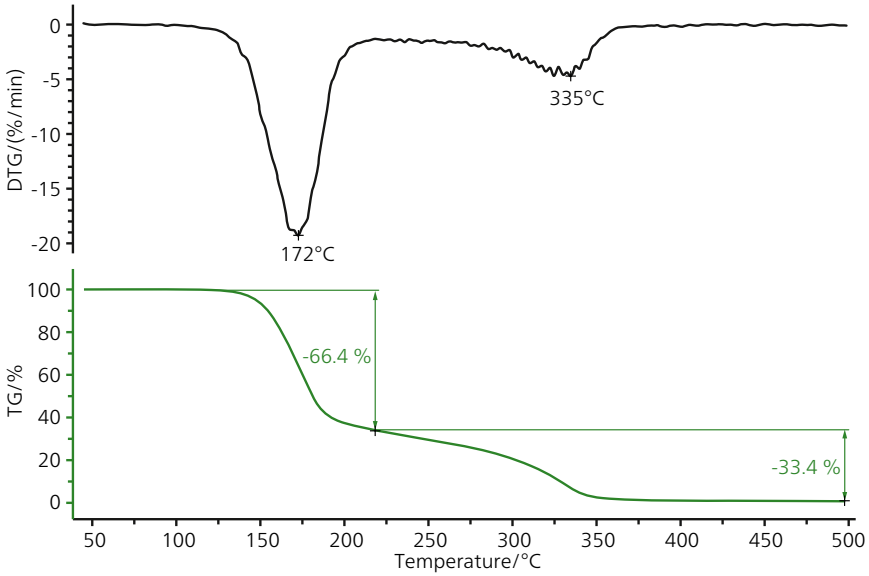
TGA curve (green) for aspartame under inert conditions; mass loss rate (DTG, black)

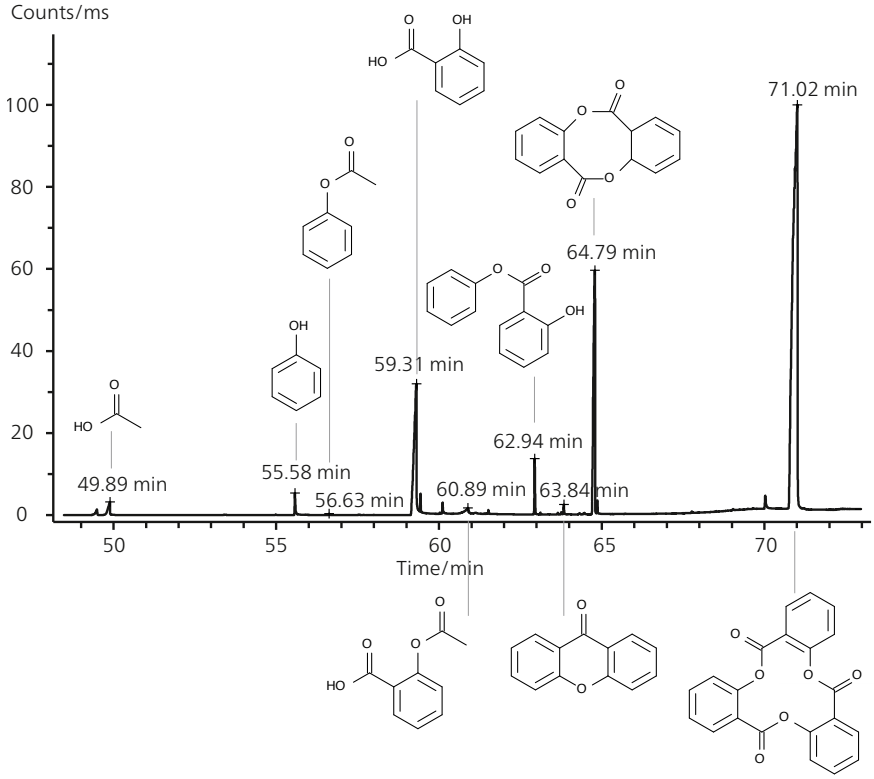


Total ion chromatogram for aspartame measured in the event mode; peaks labeled with identified compounds.



Acetylsalicylic Acid (Trade Name: e.g., Aspirin®)





The thermal behavior of a powdered acetylsalicylic acid was studied in a helium atmosphere. The gases released during evaporation or decomposition reactions were sampled at 1-min intervals on the cryo trap and subsequently analyzed by GC-MS analysis.

A look at the chromatogram reveals that at least 9 different compounds were released. Comparison with the library yields a clear identification of these compounds.

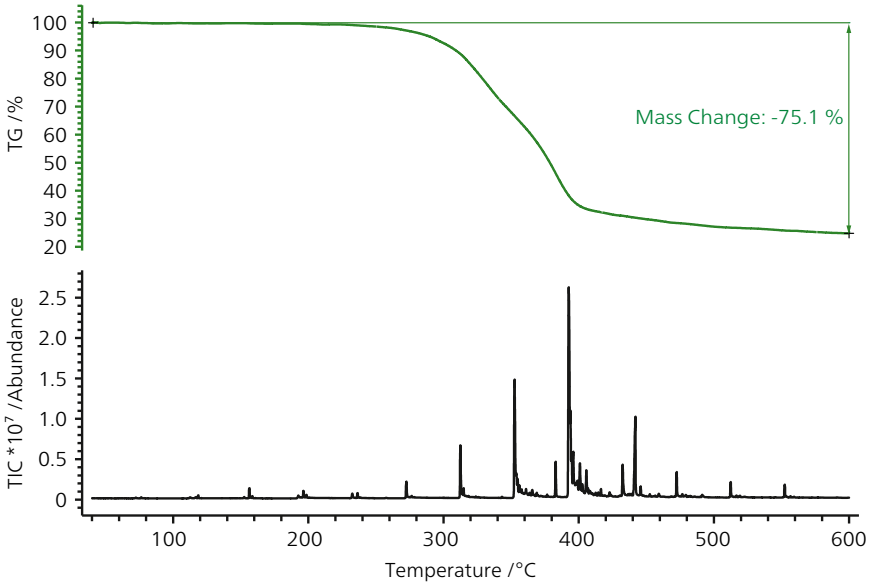
The gas mixture consists of a mixture of vaporization products (acetylsalicylic acid and its di- and trimer) along with decomposition products from smaller fragments of the acetylsalicylic acid.

Pyrolysis is the most effective way to convert biomass to bio-char, liquid bio oil, syngas, chemicals and other useful products. GC-MS coupled with thermal analysis is an elegant means of creating optimized temperature programs for pyrolysis and studying pyrolysis products.

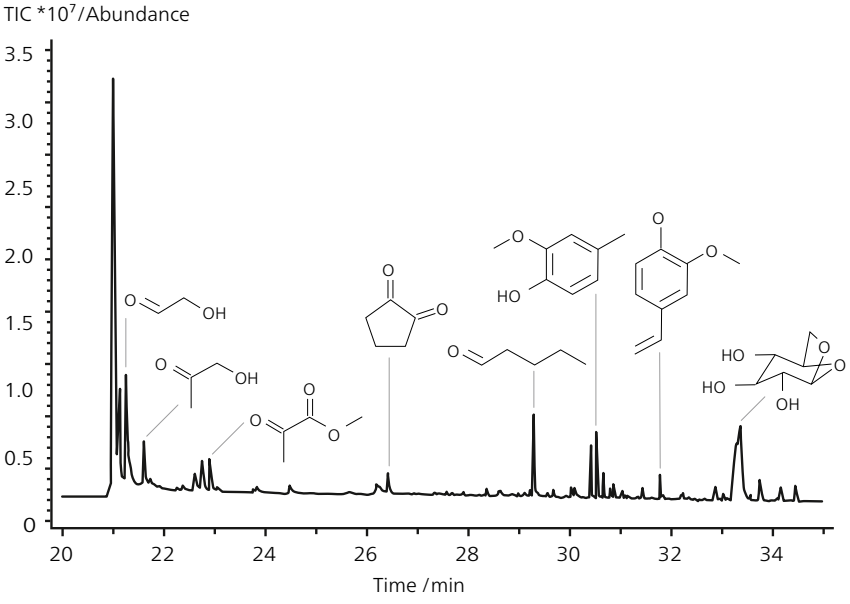
Pyrolysis of Biomass

In this example, cherry wood (3.1 mg) was pyrolized at a heating rate of 20 K/min in a helium atmosphere. The GC-MS measurement was run in the quasi-continuous mode. Between 250°C and 450°C, the TGA signal shows a mass-loss step of 75.1%. The resulting complex gas mixture was separated by the GC column and analyzed by the MS. Recurrent injections of gas samples to the GC (every 2 minutes) gave an overview of the composition of the pyrolysis gas produced.

To identify the components released, a single injection of gas was applied at the maximum of the mass-loss rate (385°C) by repeating the measurement in the event-controlled mode. The resulting total ion chromatogram (TIC) with peaks over the entire range of retention times can be easily evaluated with the help of the library search; some exemplary database hits are shown.



Wood: Temperature-dependent mass changes (TGA) and total ion chromatogram (TIC) measured in the quasi-continuous mode of the STA-GC-MS.



Total ion chromatogram (TIC) measured in the event-controlled mode; sample gas mixture taken at 385°C.

Technical Specifications

GC-MS Coupling	
Mass Spectrometer	
Manufacturer	Agilent, Jeol and others
Mass range	>1000
Mass resolution	Unit mass (adjustable by tuning)
Ionization energy	Standard 70 eV (selectable range: 5 to 241.5 eV)
Scan rates	>20000
Gas Chromatograph	
Manufacturer	Agilent and others
Valve box	▪ Heatable up to 350°C ▪ Sampling loop 250 µl or 500 µl ▪ Optional two loops
Injector	▪ Split, splitless, pulsed split ▪ Max. 450°C
GC column	▪ Standard HP-5ms column ▪ Length 30 m ▪ Max. 325°C ▪ Exchangeable
Transfer System from TGA or STA	
Heated furnace adapter	Max. 400°C
Heated transfer line	Glass-lined steel pipe max. 350°C
Length of transfer line	1.5 m (other lengths on request)
Bypass system for excess gas at the furnace	Yes

Coupling to existing NETZSCH devices of the series TGA, DSC, STA, DIL and TMA is possible. Please, contact your NETZSCH sales representative for details.


NETZSCH Thermokinetics
Curing of Epoxy Resin
Heat flow rate/(W/g)
0
-0.5
-1.0
-1.5
-2.0
-2.5
20.4 K/min
10.1 K/min
5.0 K/min
150
Temperature/°C

Expertise in Service

Our Expertise – Service

All over the world, the name NETZSCH stands for comprehensive support and expert, reliable service, both before and after sale. Our qualified personnel from the technical service and application departments are always available for consultation. In special training programs tailored for you and your employees, you will learn to tap the full potential of your instrument. Choose your preferred training method: Online, on-site or at our NETZSCH training center.

To maintain and protect your investment, you will be accompanied by our experienced service team over the entire life span of your instrument.

Our Expertise – Applications Laboratories

The NETZSCH Thermal Analysis applications laboratories are a proficient partner for nearly any Thermal Analysis issue. Our involvement in your projects begins with proper sample preparation and continues through meticulous examination and interpretation of the measurement results. Our diverse methods and over 30 different state-of-the-art measuring stations will provide ready-made solutions for all your thermal needs.

Within the realm of thermal analysis and the measurement of thermophysical properties, we offer you a comprehensive line of the most diverse analysis techniques for materials characterization.

Measurements can be carried out on samples of the most varied of geometries and configurations. You will receive high-precision measurement results and valuable interpretations from us in the shortest possible time. This will enable you to precisely characterize new materials and components before actual deployment, minimize risks of failure, and gain decisive advantages over your competitors.

TECHNICAL SERVICE

- Maintenance and Repair
- Software Updates
- Exchange Service
- IQ/OQ Documents
- Calibration Service
- Spare Part Assistance
- Moving Service

TRAINING

- Basic Seminars
- NETZSCH Online Academy
- Comprehensive Instrument and Method Training

LABORATORY

- Application Service and Contract Testing

The NETZSCH Group is an owner-managed, international technology company with headquarters in Germany. The Business Units Analyzing & Testing, Grinding & Dispersing and Pumps & Systems represent customized solutions at the highest level. A worldwide sales and service network ensure customer proximity and competent service.

Our performance standards are high. We promise our customers Proven Excellence – exceptional performance in everything we do, proven time and again since 1873.

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